



Minimization of the deactivation of palladium catalysts in the hydrodechlorination of trichloroethylene in wastewaters

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ABSTRACT

The deactivation of carbon- and alumina-supported palladium catalysts used for trichloroethylene (TCE) hydrodechlorination in wastewaters at mild conditions is studied in this work. TCE concentrations are in the interval of industrial wastewaters (200–900 ppm, corresponding to 1.54–6.92 mmol/L). Reaction studies have been performed in both batch slurry reactor and continuous fixed bed reactor. In both cases, a deactivation model (considering first-order kinetics for the main reaction, first-order deactivation kinetics, and the residual activity of the deactivated catalyst) has been proposed and experimentally validated. In general terms, carbon-supported catalysts are the most stable. Deactivation behavior can be explained in terms of the aqueous-phase redox and complexation equilibria of the active phase. The effect of different operation approaches, such the modification of the pH or the addition of alkalinity sources has been tested, being observed that the addition of sodium carbonate largely increases the catalyst stability.

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1. Introduction

Industrial wastewaters containing organochlorinated pollutants are an important environmental and toxicological hazard [1]. Specifically, trichloroethylene (TCE) is widely used in industrial applications, such as metal degreasing. Large amounts of chlorinated pollutants are released to the environment, from this kind of applications. It should be noted that the solubility of this compound (1100 ppm; 8.46 mmol/L) is higher than that corresponding to other chlorinated compounds, such as polychlorobenzenes or most of the polychlorophenols. Thus, wastewaters with concentrations of TCE close to the saturation value are released during the rinsing of the metallic surface and the cleaning of the industrial facilities [2,3].

Regarding the treatment of these wastewaters, catalytic hydrodechlorination (HDC) should be considered as a valid alternative, since it is a clean, relatively cheap, and efficient technique, the treatment being possible even at ambient temperatures [4,5]. During the HDC reaction, the chlorinated pollutant is quantitatively transformed into non-halogenated hydrocarbon and hydrogen chloride. This technology has been proved to be efficient for the treatment of chlorinated organic wastes [6–8] and gaseous emissions [9], even in air, after an adsorption enrichment procedure [10]. Concerning non-aqueous

liquid phase hydrodechlorination, it has been studied using organic solvents and hydrotreating catalysts ([11] and references cited therein), or even in the absence of solvent (for example in the selective HDC for transforming tetrachloromethane into chloroform [12]). Most of the studies reported in the literature about aqueous-phase hydrodechlorination processes are focused on polluted groundwater, with very low concentration of chlorinated pollutants (about 1–10 ppm) [13–15]. At this point, it has been demonstrated that, even from an economic point of view, hydrodechlorination processes are better than other physico-chemical processes, such as adsorption or, less markedly, air stripping [16]. Although less studied, the operation with higher TCE concentrations could be an interesting alternative approach, since it allows the treatment of the polluted water where it is generated, avoiding the spreading of the environmental problem.

The most usual catalysts used for HDC reactions are noble metals supported on alumina or activated carbons [6,7], palladium being the most common active phase. The main problem in the use of these catalysts in aqueous-phase reactions is the catalytic deactivation, specially caused by the poisoning effect of the protons and chloride ions released during the reaction [17], as well as the leaching of the active phase promoted by these ions [18]. These effects become more important in industrial wastewaters, with concentrations of chlorinated compounds close to the saturation (1100 ppm in the case of trichloroethylene, the chlorinated pollutant most often found in these wastes [2,3]). On the other hand, the deactivation of palladium catalysts has been widely studied for gas-phase reactions ([17] and references cited

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therein), but it has been less thoroughly studied in the case of aqueous-phase hydrodechlorination reactions. At this point, there are authors who suggest that the hydrogen chloride released during the reactions does not have any noticeable effect [19], whereas other authors [20] claim that this effect is important even at very low reactant concentrations (10 ppm). In works carried out with higher pollutant loadings, the deactivation effects are more important, although there is no agreement about the deactivation mechanism: poisoning [21] or leaching [18]. It is also accepted that the support plays a key role on the deactivation behavior, and that the presence of strong bases may mitigate these effects [15,18]. However, there are, to the best of our knowledge, neither systematic attempts to understand the chemical phenomena involved in the catalyst deactivation, nor development of mathematical models accounting for these effects. In addition, most of these works are carried out in batch reactors, whereas continuous flow reactors are more appropriate for establishing deactivation causes.

Therefore, this work is focused on the study of the stability of the catalyst for the treatment of these wastewaters. Specifically, the effect of the support, as well as the effect of the addition of external chlorides, bases (NaOH or chemical buffers) and alkalinity (addition of Na_2CO_3) on the catalyst performance has been studied. The studies have been carried out both in batch and in continuous fixed bed reactor, deactivation models being proposed for both cases.

2. Experimental

2.1. Materials

Three commercially available palladium catalysts: ESCAT 142 and ESCAT 14, 5% of Pd on activated carbon and γ -alumina, respectively; and ESCAT 18, 0.5% of Pd on activated carbon (all of them kindly supplied by Engelhard) have been used in this work. Catalysts were reduced with pure hydrogen at 673 K for 7200 s in a fixed bed reactor ($W/F_{\text{H}_2} = 2500 \text{ g}_{\text{cat}} \text{ s/mol}_{\text{H}_2}$), and kept under inert atmosphere before use. Main properties of the reduced catalysts are listed in Table 1. Trichloroethylene (Panreac, analytical grade) was used to prepare synthetic wastewaters using distilled water as solvent. The use of tap water has been discarded in order to ensure reproducible properties of the reaction feed. All the chemicals used for modifying the properties of these wastewaters (sulphuric acid, nitric acid, sodium chloride, sodium carbonate, sodium-dihydrogen phosphate, disodium-hydrogen phosphate and sodium hydroxide) were of analytical grade and supplied by Panreac.

Reaction gases (H_2 as reactant, and N_2 as purge gas), and chromatographic gases (He) were supplied by Air Products – Carburros Metálicos with purity higher than 99.999%, and used without further purification.

Table 1
Palladium catalysts used in the present work.

Catalyst	Metal loading	Surface area ^a (m^2/g)	Average Pd crystallite size ^b (nm)
ESCAT 142	5% Pd/C	900	18
ESCAT 14	5% Pd/ Al_2O_3	110	21
ESCAT 18	0.5% Pd/C	1000	12

^a Measured by nitrogen physisorption at 77 K in a Micromeritics ASAP 2020. Surface area calculated according to the Method of Brunauer, Emmet and Teller.

^b Calculated from transmission electron microscopy (TEM), in a JEOL JEM2000EXII microscope. Average of at least 50 particles was considered. Further details about calculation procedures are given in Ref. [17].

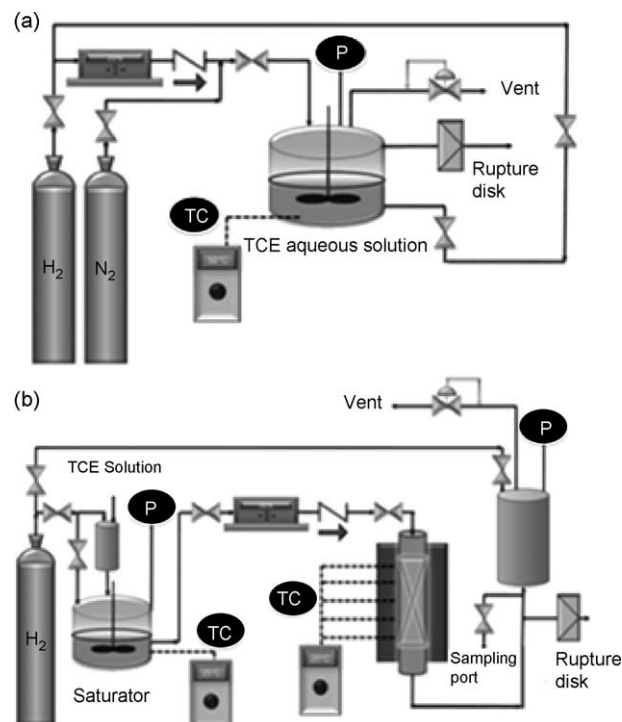


Fig. 1. Schematic drawing of the experimental set-up used for the batch experiments (a) and for the continuous experiments (b).

2.2. Experimental procedure

Two kinds of experiments were carried out in this work. The first one was carried out in a 1 L stirred batch autoclave reactor (Autoclave Engineers) equipped with a PID temperature controller and a back-pressure regulator, whereas a fixed bed solid–liquid reactor was used for the second one. Both set-ups are schematically shown in Fig. 1. For the first set of experiments, the reactor was loaded with the synthetic wastewater (0.5 L, containing trichloroethylene and the externally added compounds, such as NaCl, H_2SO_4 , HNO_3 , NaOH, Na_2CO_3 or phosphate buffers) and the corresponding amount of catalyst (typically 200 mg, with an average particle diameter of 10 μm). Then, the reactor was purged with pure nitrogen, in order to remove dissolved air. When the sample reaches the desired reaction temperature (this time period is always lower than 1800 s), the reactor is pressurized with hydrogen up to 5 MPa, ensuring the presence of a stoichiometric excess of hydrogen ($\text{H}_2/\text{TCE} > 10$ in all the cases). At this moment, an initial sample is taken, analyzed (according to the procedure described in the following paragraphs) and the concentration of this sample used as the initial concentration for further calculations. Concentration of TCE at the experiment beginning was close to 900 ppm (6.92 mmol/L). Separate experiments, increasing this contact time up to 4 h, provide similar value of TCE concentration, suggesting that the adsorption capacity of the solid is completely saturated after these 1800 s. The hydrogen pressure was kept constant during all the experiments by connecting the reactor to a continuous hydrogen flow and a pressure regulator.

In the case of the experiments carried out in the continuous fixed bed reactor, the autoclave reactor is used as saturator, the autoclave pressure being fixed in order to get H_2/TCE molar ratios of 10:1. The operation at pressures higher than 0.5 MPa leads to inaccurate analysis because of the stripping of chlorinated compound during the sample withdrawal. In order to work at these conditions under the above-mentioned H_2/TCE molar ratio, lower values of the TCE initial concentration were used (around

20% of the saturation value). Gas-saturated liquid was fed to a fixed bed reactor, placed in a thermostatic water bath in order to fix the reaction temperature, with a mass-flow regulator (Bronkhorst High-Tech L1C2-FAD-22-K). In these experiments, a flow rate of 0.017 mL/s, and catalyst weight of 100 mg (250–350 μm particle size) of the catalysts – with a 0.5% Pd loading – was used (corresponding to a space time of 3.2×10^6 s g/mol).

Samples taken in both devices were analyzed in a gas chromatograph (Shimadzu GC-17A), equipped with a 30 m HP5 chromatographic column and an ECD detector (Shidzu ECD-17). The samples (2 mL) were extracted with diethylether (1 mL) prior to analysis. Dichlorobenzene was used as internal standard in the chemical analysis. The total concentration of chloride ions in the medium has been determined using a chloride selective electrode (Crison 9652). Chlorine mass balance was checked in order to ensure the correctness of the measurements and the absence of adsorption or volatilization phenomena.

The absence of both internal and external mass transfer effects in the experiments reported in this work has been both experimentally and theoretically demonstrated, as described in detail elsewhere [22]. Experimental tests consisted of replying experiments with different particles sizes in both the batch reactor and fixed bed reactor; and changing simultaneously – at constant space time – the catalysts loading and the flow rate in the packed bed reactor. In summary, the theoretical approach consisted of deriving a kinetic model considering the gas–liquid mass transfer (only in the batch reactor), the liquid–solid mass transfer and the Thiele modulus-based efficiency factor for internal diffusion. Transport coefficients were estimated according to the isotropic turbulence model of Kolmogoroff (liquid–solid interface in the batch reactor) [23], the Frosslig equation (for liquid–solid interface in the fixed bed reactor) [24], and the equation proposed by Hoffer et al. for hydrogenation in slurry reactors (gas–liquid interface) [25]. Concerning the Thiele modulus, its average value for the experiments reported in this work (considering first-order kinetics, and effective diffusion in the order of 10^{-9} m²/s), were five orders of magnitude lower than unity, it being possible to neglect the effect of the internal diffusion in the overall kinetic equation. If the denominator of reaction rate equation is considered as a sum of additive resistances (associated to gas–liquid transport, liquid–solid transport and chemical reaction, respectively), the value of the last resistance account for more than 95% in all the experiments reported in this work.

3. Results and discussion

3.1. Experiments in the batch slurry reactor

The first set of experiments, carried out with 200 mg of Pd/Al₂O₃ (5%Pd) and a TCE concentration of 900 mg/L (6.92 mmol/L) are depicted in Fig. 2, where the evolution of the conversion with the reaction time at different temperatures (in the interval 293–323 K) is shown. Similar experiments were replicated at the highest temperature, but working without catalyst and adding 200 mg of activated carbon. In both cases, the conversions obtained were negligible, suggesting that the reaction proceeds through a catalytic mechanism. Selectivities to non-chlorinated compounds were higher than 99%, mass balance being checked in terms of chlorine balance. Detailed analysis of both the liquid phase and the gas head space discarded the presence of partially dechlorinated compounds. Concerning the ethane/ethylene molar ratio, values higher than five were obtained in all the reported experiments.

It is observed that the conversion reaches a plateau below 100%. This result indicates the presence of important deactivation phenomena. In order to determine these effects quantitatively, a

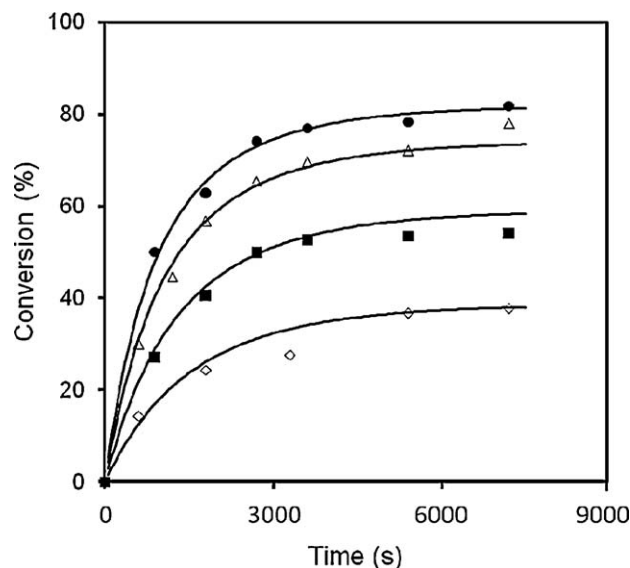


Fig. 2. Trichloroethylene conversion as a function of reaction time ($C_0 = 6.92$ mmol/L, $P_{H_2} = 5$ MPa, $W_{cat} = 0.2$ g) for the 5% Pd/Al₂O₃ catalyst. Reaction temperature: 293 K (\diamond), 303 K (\blacksquare), 313 K (\triangle) and 323 K (\bullet). Lines correspond to model prediction according to Eq. (2).

deactivation model has been proposed. This model considers that the main reaction presents a pseudo-first-order dependence on TCE and a zero-th order dependence on H₂ and all the reaction products. Although is widely accepted that hydrodechlorination reactions follow Langmuir–Hinshelwood mechanisms [8,26], the behavior can be assumed as first-order kinetics in a wide range of operation conditions, especially in aqueous-phase conditions and when only one chlorinated compound is being hydrogenated. Deactivation phenomena have been introduced considering a Szepe–Levenspiel [27] deactivation rate expression, and assuming that the activity variation follows a first-order dependence on activity (that is, considering independent deactivation, according to the Levenspiel classification). Therefore, the behavior of the reacting system will be described by this set of equations:

$$\begin{cases} -r_{TCE} = k_v C_{TCE} a \\ -\frac{da}{dt} = k_d a \end{cases} \quad (1)$$

where C_{TCE} is the TCE concentration (mol/L), $-r_{TCE}$ the reaction rate (mol/L s), a the activity (dimensionless and with $0 < a < 1$), and k_v and k_d (both in s⁻¹) the kinetic constants for the hydrodechlorination and the deactivation, respectively. Integrating the equations, a simplified expression is obtained:

$$\ln \ln \frac{C_{TCE}}{C_{TCE,\infty}} = \ln \frac{k_v}{k_d} - k_d \times t \quad (2)$$

where $C_{TCE,\infty}$ is the concentration of TCE extrapolated at infinite time. The goodness of the fit is observed in Fig. 3a. This equation allows the estimation of the activation energy for both the main reaction and the deactivation process, supposing that both kinetic constants follow Arrhenius dependence (Fig. 3b and Table 2). The value of the activation energy for the main reaction (30 kJ/mol) is in good agreement with the values reported in the literature for this kind of reactions. So, Kovenklioglu et al. [28] reported a value of 32 kJ/mol for the aqueous-phase hydrodechlorination of TCE over Pd/C catalysts. Even when the TCE hydrodechlorination is carried out in gas phase, activation energies reported in the literature are similar (35–38 kJ/mol) to those determined in this work [8]. Concerning the deactivation, it is observed that its kinetic constant remains almost unaffected when the temperature

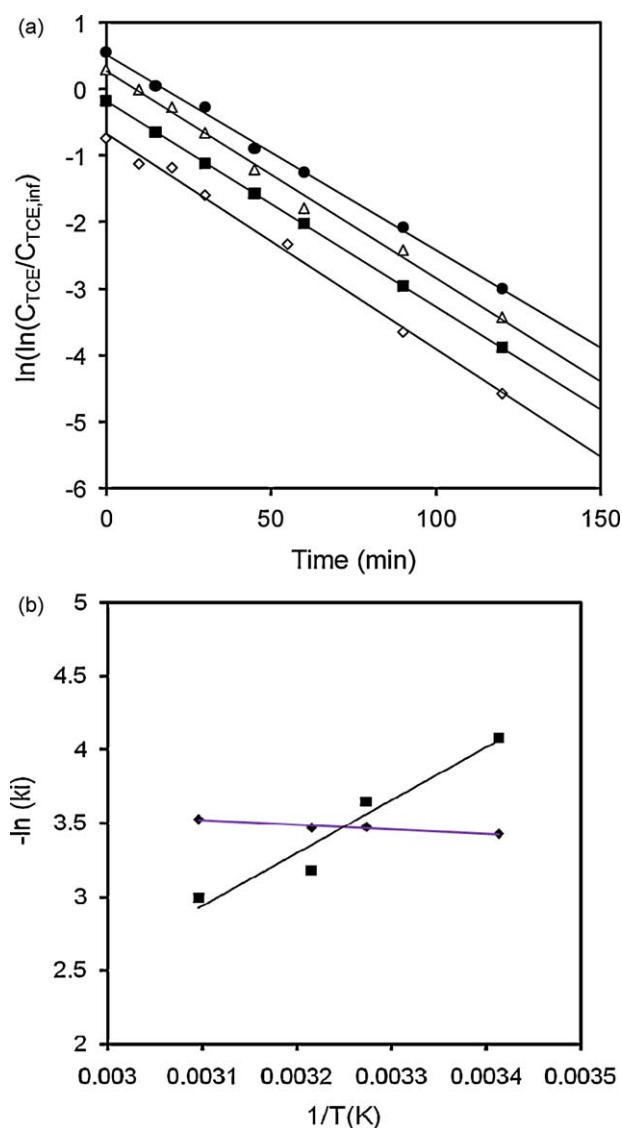


Fig. 3. (a) Deactivation modeling results for the experiments carried out in the batch reactor with Pd/Al₂O₃ catalyst. See codes in Fig. 2. (b) Arrhenius plots for the evolution of kinetic constants, k_d (◆, s^{−1}) and k_v (■, s^{−1}), with temperature.

increases (apparent activation energy of −2 kJ/mol). This result is very interesting since it would allow compensating the deactivation of the catalyst by an increase in the operation temperature.

Typical poisoning behavior involves two successive steps: the adsorption of the poisonous agent on the catalyst active sites and the reaction of the poisonous molecule with these sites. The second one is usually kinetically controlled yielding to positive activation energies, whereas the first one can be equilibrium controlled, being the adsorption process slightly exothermic, yielding to negative apparent activation energies [29]. Our results suggest that both steps are partially compensated, yielding an apparent activation energy close to zero.

At first insight, the good fitting obtained considering independent deactivation is unexpected considering that, as it will be discussed later, protons and chloride anions play a key role on catalyst deactivation. However, it must be taken into account that the effect of these ions depends on their surface concentration (θ_i), a Langmuir-type adsorption equilibrium being considered. Therefore, the goodness of our fit suggests that the interaction of these ions with the active phase is strong, which, according to the Langmuir theory will lead to formal zero-th order on poison concentration. Similar behaviors are reported in the literature for catalytic reactions with strong deactivation effects, such the hydrogenolysis of organo-nitrogen compounds over acid catalysts [30]. More complex models, considering that deactivation rate also depends on the concentration of the involved species, have also been tested, providing worst fitting in spite of the higher mathematical complexity of the expressions.

The first strategy to be considered in order to overcome this deactivation is the addition of chemical products that can minimize the effect of the poisonous substances released during the reaction. Xia et al. [31] reported that the addition NaOH mitigates the deactivation during the aqueous-phase hydrodechlorination of chlorophenols, whereas Yuan and Keane [32] stated that NaOH is better for this purpose than the other alkaline hydroxides. However, it should be noted that carbonate ions could have the same effect (neutralizing the protons released during the reaction) as that of the hydroxide ions, but without changing the pH conditions so drastically.

Taking into account these facts, deactivation experiments in the batch reactor were repeated adding 40 mmol/L of sodium carbonate. Obtained results (Fig. 4) show that the addition of this alkalinity source has a positive effect on the catalysts performance, although deactivation still takes place to some extent. The observed deactivation behavior can be modeled using the same approach that in the previous case. Modeling results (summarized in Fig. 4b and in Table 2) show that the kinetic parameters of the main reaction remain unaltered, whereas deactivation constants are lower in this case, presenting slightly positive activation energy.

Concerning the experiments carried out in the batch reactor with the Pd/C catalysts, no deactivation was observed, the conversion–time curve showing the typical profile of first-order kinetics without deactivation (Fig. 5). The addition of sodium carbonate, at the same concentration as that in the experiments reported before, does not have any noticeable effect on the catalyst performance. Therefore, any poisonous effect of this compound can be discarded. At this point, McNab and Ruiz [33] stated that carbonates and bicarbonates can be reduced over Pd catalysts, yielding formate species, which can inhibit hydrodechlorination. However, these species have not been observed in our experiments. In order to determine the effect of the pH on the catalyst performance, hydrodechlorination experiments were also conducted at very low pH, accomplished with the addition of strong mineral acids. Results obtained with sulphuric acid, at pH 1, are also shown in Fig. 5. It is observed that the presence of this compound leads to important deactivation effects, characterized by the plateau observed at low conversion. This experiment was replicated using HNO₃ instead of H₂SO₄ as acidity source (also

Table 2

Summary of the kinetic data obtained for the experiments carried out in the slurry batch reactor. R is expressed in kJ/mol.

Catalyst	Operation conditions	k_v (s ^{−1})	k_d (s ^{−1})
Pd/Al ₂ O ₃	No external additives	$2.7 \times 10^{-4} \exp(-(30/RT))$	$87 \exp(+2.5/RT)$
Pd/Al ₂ O ₃	Na ₂ CO ₃ (40 mM)	$3.6 \times 10^{-5} \exp(-(36/RT))$	$6.4 \exp(-(6.5/RT))$
Pd/C	No external additives	7.01×10^{-4} (T = 293 K)	Not observed
Pd/C	Na ₂ CO ₃ (40 mM)	6.99×10^{-4} (T = 293 K)	Not observed
Pd/C	H ₂ SO ₄ (pH 1)	5.99×10^{-4} (T = 293 K)	4.72×10^{-4} (T = 293 K)

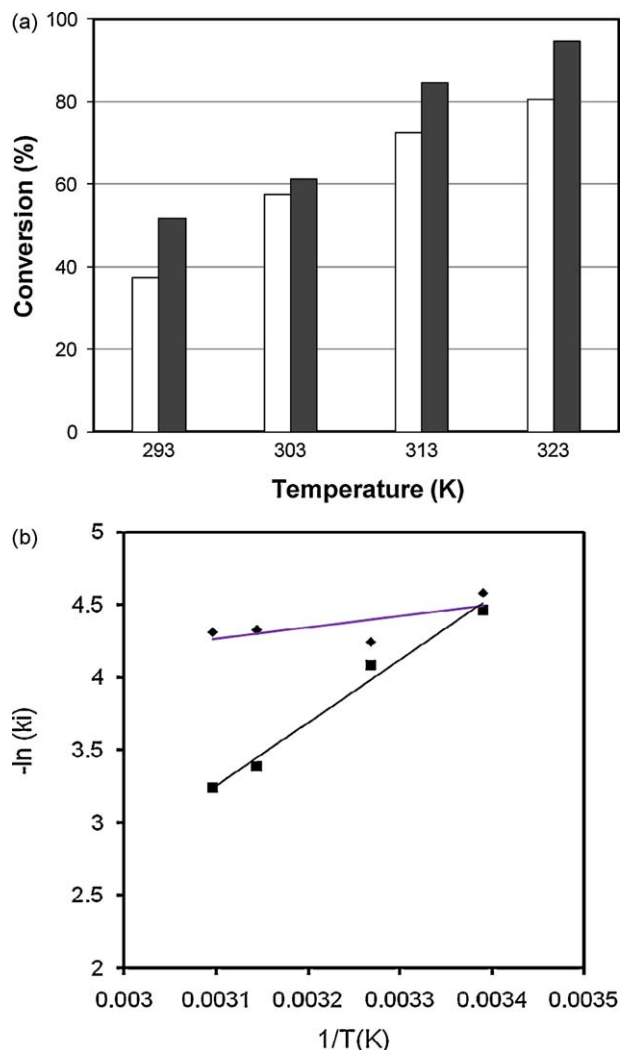


Fig. 4. (a) Comparison of the activity of the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst for TCE hydrodechlorination after 6 ks reaction time in absence (white bars) and in presence (black bars) of Na_2CO_3 (40 mmol/L). For operation conditions see Fig. 2. (b) Arrhenius plot for the evolution of kinetic constants, k_d (\diamond , s^{-1}) and k_v (\blacksquare , s^{-1}), with temperature for the experiments carried out in presence of Na_2CO_3 .

working at pH 1), obtaining the same results and discarding any additional poisoning because of the sulphate ions. It is also accepted (see for example the recent work of Munakata and Reinhard [34]) that the poisonous effect of sulphur compounds is caused by reduced species, such as sulphites or sulphides. At this point, even catalyst regeneration is observed when sulphur-poisoned catalysts are treated with oxidants that promote sulphate formation [35,36].

3.2. Experiments in the continuous fixed bed reactor

A set of experiments was carried out in a continuous fixed bed reactor (at 298 K) with the aim of getting a better understanding of the deactivation phenomena taking place during the aqueous-phase hydrodechlorination over palladium catalysts. In order to be able to follow a wide range of conversions, a carbon-supported palladium catalysts with a lower metal loaded (0.5%) was selected. The experiments were carried out at 0.5 MPa, with a total concentration of TCE of 250 ppm (1.92 mmol/L), and a space velocity (WHSV) of 600 h^{-1} , corresponding to a space time ($W/F_{\text{TCE},0}$) of 3.2×10^6 (s g/mol of TCE). The operation pressure in the saturator and therein in the reactor was selected in order to ensure

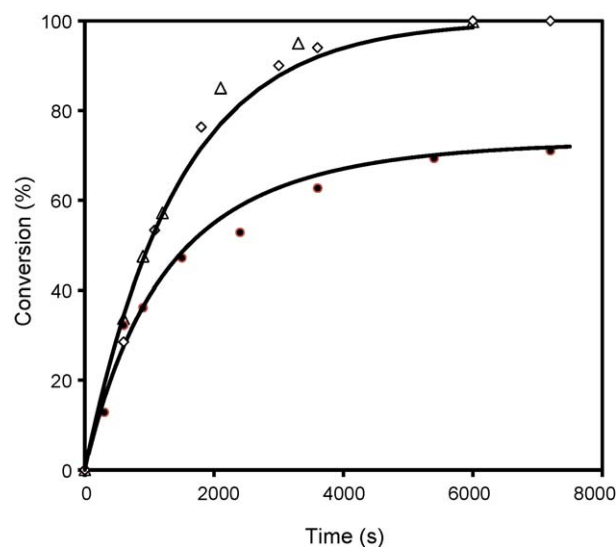


Fig. 5. Trichloroethylene conversion as a function of reaction time ($C_0 = 6.92 \text{ mmol/L}$, $P_{\text{H}_2} = 5 \text{ MPa}$, $W_{\text{cat}} = 0.2 \text{ g}$, $T = 293 \text{ K}$) for the 5% Pd/C catalyst. Experiments were carried out without any external additive (\triangle), in presence of 40 mmol/L of Na_2CO_3 (\diamond) and in presence of H_2SO_4 (\bullet , pH 1). Lines correspond to model prediction according to Eq. (2).

that the hydrogen is a great excess ($\text{H}_2/\text{TCE} > 10$ in all the experiments), not affecting the measured kinetics.

The results obtained in the parent experiment; working with an aqueous solution of TCE, without any other external additions are depicted in Fig. 6. It is observed that the catalyst presents a marked deactivation in the first reaction hours, reaching a period of non-negligible constant activity after this period. The differences between the behavior of the carbon-supported catalysts in the batch and in the continuous reactor can be strange at first insight. However, these differences could be explained if it is assumed (as it will be explained later) that the deactivation cause is the reaction of the protons with the active phase. Therefore, catalyst deactivation will depend on the exposure period (time on stream for continuous experiments, and reaction time for batch experiments), TCE concentration and obtained conversion. Although both experiments were performed keeping similar TCE loadings, expressed as mol of TCE treated by Pd atom and second

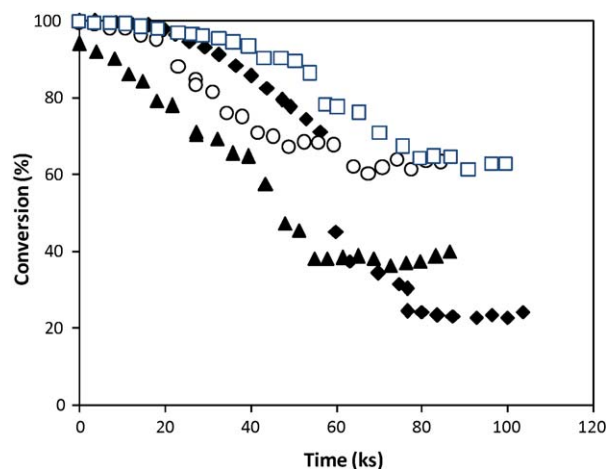


Fig. 6. Deactivation curves for the experiments carried out in the fixed bed reactor with the 0.5% Pd/C at 298 K ($W_{\text{cat}}/F_{\text{TCE},0} = 3.2 \times 10^6 \text{ s g/mol}_{\text{TCE}}$). Effect of different matrices on catalyst performance: experiment without any external addition (\diamond), experiment with 40 mmol/L of Na_2CO_3 (\square), experiment with phosphate buffer solution (\circ) and experiment with 40 mmol/L of NaOH (\blacktriangle).

(5.9 $\mu\text{mol}/\text{Pd atom s}$ for slurry reactor and 6.8 for fixed bed reactor) the average conversions are largely higher in the continuous reactor, so that higher amount of H^+ and Cl^- are released from the beginning of each experiment.

As the aqueous-phase reduction yields chloride ions and protons, the effect of both species on the catalyst performance must be separately studied. There is not agreement in the literature about the effect of these factors. So, the group of Schüth [37], claimed that the chloride ions have not any noticeable effect on catalyst stability, whereas Perrone et al. [20], working with the same concentration of TCE, suggested the opposite behavior. Concerning the effect of the pH, the most of the works report that pH increases by addition of strong bases (such as alkaline hydroxides) have a positive effect on the catalyst stability [32,38]. For practical application, the use of other species that can react with the protons but do not cause so larger pH increases will be of great interest.

Three different approaches for scavenging the protons released in the reaction have been considered:

- (1) The increase of the pH of the reaction media just by adding an alkaline hydroxide.
- (2) Working at controlled pH, using a buffer solution. Phosphate/hydrogenophosphate solutions are the most common buffers proposed in the literature [39]. In this case a 0.008 mol/L of a NaH_2PO_4 and 0.1136 mol/L of Na_2HPO_4 solution was used, resulting in a pH of 7.5.
- (3) Use of an alkalinity source. The role of the alkalinity is, in addition to increase the pH medium, to provide anions (as CO_3^{2-}) which can react with the protons released during the reaction, yielding bicarbonate ions.

Three different experiments were performed working with a solution with 40 mmol/L of NaOH (initial pH of 13.2), another with a phosphate-buffered solution (initial pH of 7.5), and a last one with a concentration of Na_2CO_3 of 40 mmol/L (initial pH of 11.1). Results obtained are summarized in Fig. 6. In the case of the experiment carried out in presence of NaOH, the initial conversion is lower (93% vs. 99%) and the deactivation of the catalyst is faster, although the residual conversion of the catalyst is slightly higher than in the experiment carried out without any external addition. When the phosphate buffer is used, the initial activity is unaffected (99%), the deactivation rate decreases and the residual conversion is also higher than the corresponding to the previously reported experiment. However, the most favourable case is when sodium carbonate is added. In this case, the deactivation rate is the lowest, and the residual activity is the highest of the experiments reported in this work, whereas the initial conversion is also about 99%. If our results are compared with those reported in the literature, it is observed that the presence of NaOH in the reaction media is considered to have the detrimental effect on the textural and metallic properties of the palladium catalysts, leading to worst performance [40]. These authors suggested that the addition of alkaline metals during catalysts preparation is more positive for catalyst performance [41,42].

The next parameter to be studied is the effect of the chloride ions released in the reaction. In this way, an experiment with the same concentration of TCE, the same hydrogen pressure but adding an external source of chloride ions (25 mmol/L of NaCl) has been carried out. In this experiment, the amount of chloride ions added is equivalent to five times the stoichiometric amount of Cl^- released for total TCE conversion. It is observed in this case (Fig. 7) that the catalyst is almost completely deactivated, with very low residual activity. It should be taken into account that the presence of externally added Cl^- does not affect to the initial conversion, suggesting that the effect of this anion is related with the

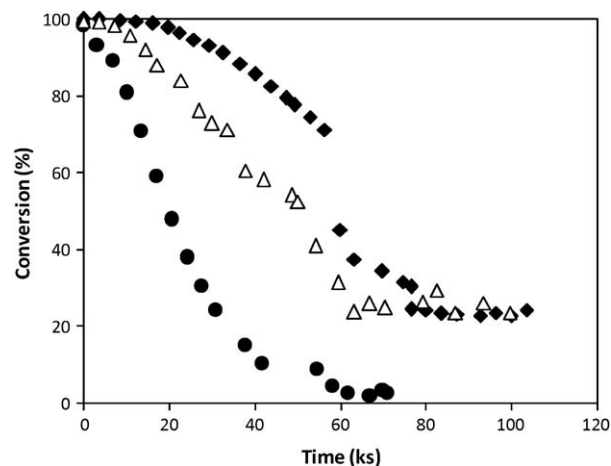


Fig. 7. Deactivation curves for the experiments carried out in the fixed bed reactor with the 0.5% Pd/C at 298 K ($W_{\text{cat}}/F_{\text{TCE},0} = 3.2 \times 10^6 \text{ s g/mol}_{\text{TCE}}$). Effect of the presence of an external source of chloride ions on catalyst performance: experiment without any external addition (\blacklozenge), experiment in presence of 25 mmol/L of external chloride ions (\bullet), and experiment in presence of 25 mmol/L of external chloride ions and 40 mmol/L of Na_2CO_3 (\triangle).

deactivation rather than equilibrium or kinetic effects. The same experiment was repeated in presence of Na_2CO_3 , being observed (also in Fig. 7) that this salt largely decreases the poisonous effects of the chloride ions. This result is of great importance, since it is well-known that Na_2CO_3 does not react with chloride ions. This

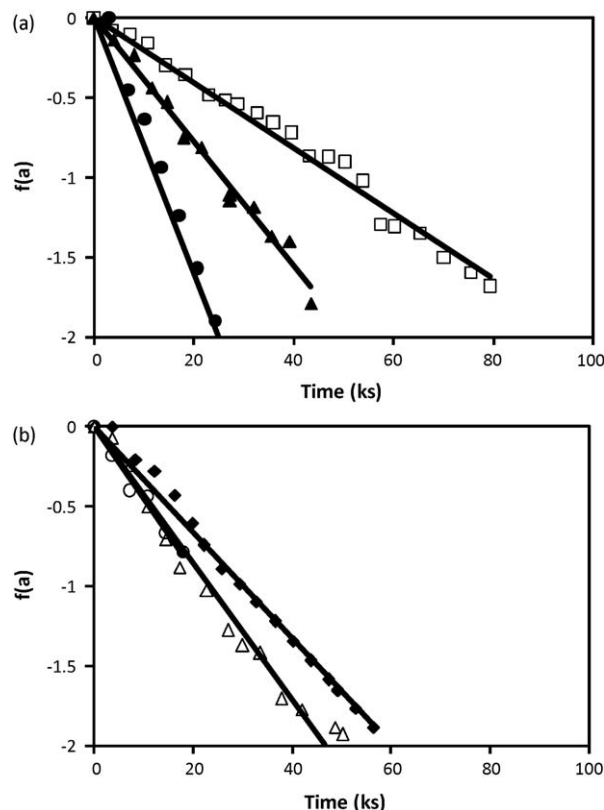


Fig. 8. Fitting results of the proposed deactivation model (Eq. (5)) for the experiments carried out in the continuous fixed bed reactor. (a) Experiment with 40 mmol/L of NaOH (\blacktriangle), experiment with 40 mmol/L of Na_2CO_3 (\square), and experiment in the presence of 25 mmol/L of external chloride ions (\bullet). (b) Experiment without any external addition (\blacklozenge), experiment with phosphate buffer solution (\circ), and experiment in presence of 25 mmol/L of external chloride ions and 40 mmol/L of Na_2CO_3 (\triangle).

effect indicates that chloride ions and protons have a synergetic effect on catalyst deactivation.

In order to systematically compare all the experiments carried out in the continuous flow reactor, a deactivation model has been derived. Since it is well accepted that the kinetics of the main chemical reaction follows a first-order dependence on TCE concentration, the activity of the catalysts at a given time can be calculated according to the following equation, derived considering integral plug flow reactor:

$$a = \frac{\ln(1-x)}{\ln(1-x_0)} \quad (3)$$

where x is the conversion at a given time and x_0 is the initial conversion. In order to take into account the residual activity of the catalyst (a_∞), the deactivation model can be expressed as:

$$-\frac{da}{dt} = k_d(a - a_\infty) \quad (4)$$

This equation can be integrated and expressed in a linear form in the following way:

$$f(a) = \ln \left[\frac{(a(t) - a_\infty)}{1 - a_\infty} \right] = -k_d t \quad (5)$$

The straightness of the plots of $f(a)$ vs. time (as depicted in Fig. 8) confirms the validity of the proposed model. The correlation coefficient (r^2) as well as the values of the kinetic parameters for all the experiments carried out in the continuous reactor are summarized in Table 3. The proposed model allows comparing the results obtained in the reported experiments in terms of both the deactivation rate constant and the residual activity, the best situations being those with the highest residual activities and lowest deactivation rate constant.

The effect of the pH on both deactivation parameters (k_d and a_∞), considering the parent experiment, and the experiments carried out in presence of NaOH, phosphate buffer and Na_2CO_3 is depicted in Fig. 9a. As general trend, it is observed that as the pH increases, the residual activity and the deactivation kinetic constant increase. The only exception to this behavior is the case of the sodium carbonate, which leads to markedly lower deactivation kinetic constant.

In the case of the experiments carried out in the presence of an external source of chloride ions (Fig. 9b), faster deactivation and lower residual activity of the catalyst were observed. These effects are largely mitigated in presence of Na_2CO_3 . This result is very important from the point of view of the industrial application, since it is observed that the addition of small amounts of sodium carbonate can minimize catalyst deactivation. It should be noted that this compound is considered as entirely non-pollutant, being both the cation and the anion common in natural environments.

The last point to be considered is the deactivation reversibility. Thus, the catalyst has been deactivated at the most deactivating conditions found in this work (presence of external chlorine and absence of alkali), and when the catalyst was completely

Table 3

Summary of the deactivation kinetic constants, and final pH for the experiments carried out in the fixed bed reactor. See operation conditions in Figs. 6 and 7 captions. Confidence intervals calculated using Scientist software (95% confidence).

Experiment	$10^5 k_d \text{ (s}^{-1}\text{)}$	a_∞	pH	r^2
Parent experiment	3.32 (± 0.08)	0.035	3.14	0.992
Phosphate-buffered	4.50 (± 0.09)	0.209	7.91	0.981
Na_2CO_3 (40 mmol/L)	2.60 (± 0.10)	0.208	11.1	0.984
NaOH (40 mmol/L)	3.88 (± 0.12)	0.177	13.2	0.986
NaCl (25 mmol/L)	9.31 (± 0.20)	0.009	3.22	0.991
Na_2CO_3 (40 mmol/L) and NaCl (25 mmol/L)	4.99 (± 0.18)	0.052	11.2	0.985

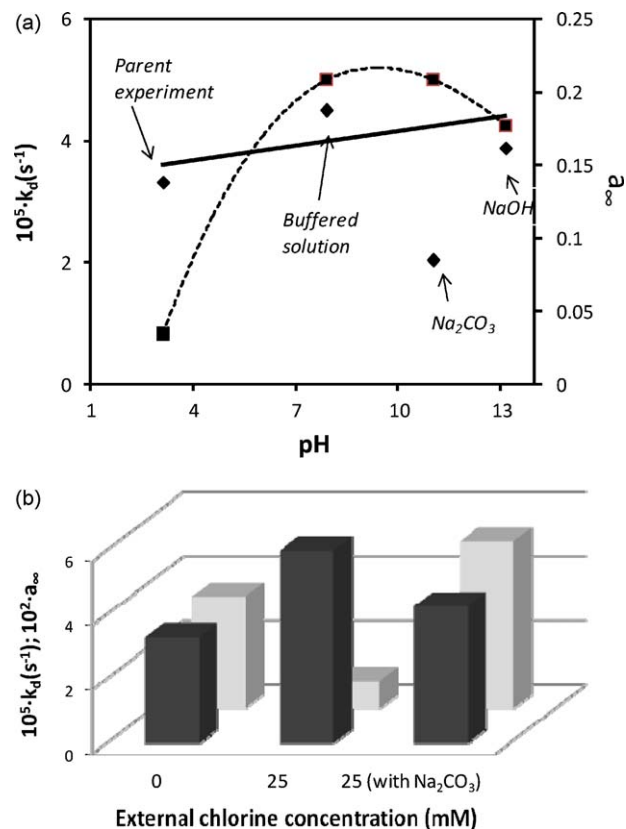


Fig. 9. Evolution of the deactivation kinetic constant (\diamond in (a) and clear bars in (b)) and residual activity (\blacksquare in (a) and dark bars in (b)) with pH (a) and presence of external chlorine (b). Experimental data correspond to the experiment carried out with the 0.5% Pd/C catalyst in the continuous fixed bed reactor.

deactivated, it was treated with distilled water (same flow rate than in the deactivation experiment for 15 h at 298 K). It is observed (Fig. 10) that when the feed is commuted again to the solution with TCE and NaCl, the catalyst has completely recovered its initial activity and shows exactly the same deactivation pattern. Therefore, deactivation of the catalysts is completely reversible.

Catalysts after being used in the deactivation experiments, as well as the fresh-reduced catalyst, were characterized by nitrogen physisorption (for determining morphological changes), transmission electronic microscopy (for detecting changes in the Pd

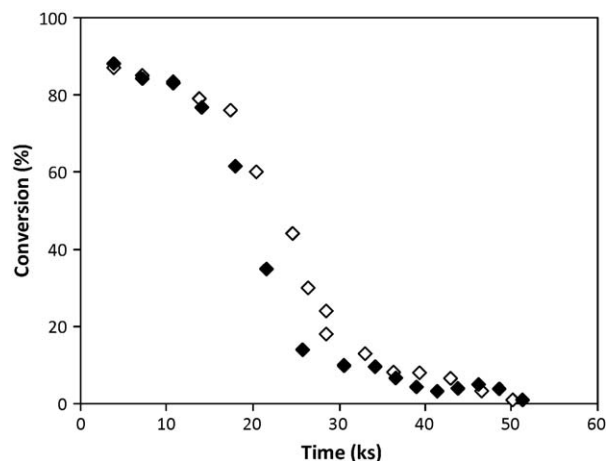


Fig. 10. TCE conversion as a function of time on stream for the experiment carried in presence of 25 mmol/L of NaCl before (\diamond) and after (\blacklozenge) the regeneration with distilled water ($T = 298 \text{ K}$, $W_{\text{cat}}/F_{\text{TCE},0} = 3.2 \times 10^6 \text{ g/mol}_{\text{TCE}}$).

crystallites size distribution) and XPS (for determining changes in the surface chemistry of the catalysts). The obtained results indicate that, as expected considering the mildness of the reaction conditions, there are neither support morphological variations nor palladium crystallites sintering. The most important finding is the absence of leaching effects. These effects are reported in the literature, especially for carbon-supported catalysts [18], but they were not observed in our case, in spite of carrying out the experiments with an excess of chloride ions. At this point, Munakata and Reinhard [34] suggest that leaching effects are important at pH values below 3, whereas all the experiments reported in this part are carried out at higher pH. XPS analyses of the fresh and used catalysts show that the fresh catalysts present a Pd^{2+}/Pd ratio, estimated according to the procedure outlined in [43], of 0.3. Although this ratio increases for the used catalyst (up to 0.6–0.75), this increase is correlated with neither the different deactivation rates nor the final activity.

In order to explain the behavior of the catalysts, the distribution of the palladium species as a function of the pH and the redox potential of the medium must be taken into account. It is widely accepted that the active phase for hydrodechlorination reactions is the reduced Pd, although small amounts of Pd^{2+} are also needed for accomplishing the reaction [44]. The only reaction between the released protons and the reduced metal likely to occur is the oxidation of the metal with the subsequent release of hydrogen. From a thermodynamic point of view, this reaction is not favoured in the presence of hydrogen ($\Delta G > 0$). However, the presence of chloride ions stabilizes the Pd^{2+} species through formation of different Pd^{2+} complexes, such as PdCl_3^- and PdCl_4^{2-} , whose stability increases at pH values lower than 7 [45]. Therefore, although the chloride ions are not able to oxidise the palladium, they can promote the oxidation through equilibrium displacement by the scavenging of Pd^{2+} ions. The effect of chloride ions on the redox properties of palladium have even been reported in the literature for gas-phase catalytic processes reactions, as well as in the palladium catalysts reduction [46]. In our case, this fact explains the strong deactivation effect caused by the chloride ions, and also explains the reversibility of the deactivation observed, since complexation processes are entirely reversible. So, when chloride ions are removed from the aqueous phase, complexation equilibria are reversed, the Pd phase becoming more stable and the initial catalytic activity being recovered. This reversibility is also the cause of the non-specificity of the increase in the Pd^{2+}/Pd ratios determined by XPS.

Concerning the effect of the pH, the formation of Pd^{2+} hydroxides also leads to the stabilization of this species, although this effect is not so marked because hydroxide can also neutralize the oxidant cation (H^+). That means that when a strong base is added to the medium, it removes the protons released in the reaction (positive effect), but it favours that the ratio of Pd^{2+} increases. By contrast, the addition of external alkalinity (for example Na_2CO_3) only promotes the first positive effect. These phase equilibria also justify the residual activity of the catalysts. At this point, the activity of the different Pd species in different reactions (such as hydrogenations, combustions, etc.) is studied in the literature. In general terms, it is accepted that the palladium chlorides are among the less active palladium phases, the formation of these species as a typical poisoning cause being reported (see for example the review of Gelin and Primet [47]), whereas hydroxides present higher conversions. Therefore, highly hydroxylated palladium catalysts present important residual activities in different reactions, such as catalytic combustions [48].

Regarding the effect of the support on the deactivation behavior, the differential behavior of alumina-supported and carbon-supported catalysts is considered to be caused by the differences in the surface acidity as well as the different affinity

between the chloride ions and these supports. So, alumina support is highly hydrophilic and can concentrate these ions in the vicinity of the active phase, whereas activated carbons present lower affinity for these anions. Concerning to the surface acidity, γ -alumina is more acid than activated carbon in terms of both acid sites concentration and strength of these sites [49,50]. This highest acidity enhances the concentration of protons in the vicinity of the active phase, promoting the oxidation of Pd to Pd^{2+} . It should also be taken into account that the affinity of the support surface for the different species involved in the reaction is very dependent on the pH. At this point, the point of zero charge (PZC) for Pd/activated carbon catalysts is in the interval 3–4, according to the measurements reported in the literature [51,52]. That means that at pH values below the PZC, the catalyst surface is, on average, positively charged, showing more affinity to chloride anions, and magnifying the effect of chloride ions on the above-mentioned poisoning effect. That is the situation of the experiments carried out in absence of Na_2CO_3 , NaOH or phosphate buffers, and this fact can also explain the mitigation effect of the addition of sodium carbonate in the experiment carried out in presence of external chlorine.

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References

- [1] Toxicological Profile for Trichloroethylene and Tetrachloroethylene; Agency for Toxic Substances and Disease Registry (ATSDR), Department of Health and Human Services, Public Health Service, Atlanta, GA, 1997.
- [2] E.M. Petrie, Metal Finish. 105 (2007) 56.
- [3] European Commission, Reference Document on Best Available Techniques for Waste Treatment, Seville. Available at <http://eippcb.jrc.es/pages/FAactivities.htm>, 2005.
- [4] K. Pirkanniemi, M. Sillanpää, Chemosphere 48 (2002) 1047.
- [5] L. Calvo, A.F. Mohedano, J.A. Casas, M.A. Gilarranz, J.J. Rodríguez, Carbon 42 (2004) 1377.
- [6] S. Ordóñez, F.V. Díez, H. Sastre, Appl. Catal. B 25 (2000) 49.
- [7] S. Ordóñez, F.V. Díez, H. Sastre, Thermochim. Acta 379 (2001) 25.
- [8] S. Ordóñez, F.V. Díez, H. Sastre, Ind. Eng. Chem. Res. 41 (2002) 505.
- [9] Z.M. de Pedro, L.M. Gómez-Sainero, E. González-Serrano, J.J. Rodríguez, Ind. Eng. Chem. Res. 45 (2006) 7760.
- [10] A. Elola, E. Díaz, S. Ordóñez, Environ. Sci. Technol. 43 (2009) 1999.
- [11] S. Ordóñez, H. Sastre, F.V. Díez, Appl. Catal. B 34 (2001) 213.
- [12] L.M. Gomez-Sainero LM, X.L. Seoane, A. Arcoya, Appl. Catal. B 53 (2004) 101.
- [13] G.V. Lowry, M. Reinhard, Environ. Sci. Technol. 33 (1999) 1905.
- [14] C. Schüth, S. Disser, F. Schüth, M. Reinhard, Appl. Catal. B 28 (2000) 147.
- [15] G. Yuan, M.A. Keane, Appl. Catal. B 52 (2004) 301.
- [16] M.G. Davie, H. Cheng, G.D. Hopkins, C.A. Lebrun, M. Reinhard, Environ. Sci. Technol. 42 (2008) 8908.
- [17] E. López, S. Ordóñez, F.V. Díez, Appl. Catal. B 62 (2006) 57.
- [18] G. Yuan, M.A. Keane, Catal. Today 88 (2003) 27.
- [19] G.V. Lowry, M. Reinhard, Environ. Sci. Technol. 34 (2000) 3217.
- [20] L. Perrone, L. Prati, M. Rossi, Appl. Catal. B 15 (1998) 241.
- [21] D. Fritsch, K. Kuhr, K. Mackenzie, F.D. Kopinke, Catal. Today 82 (2003) 105.
- [22] B.P. Padilla, Treatment of polluted wastewaters using catalytic hydrodechlorination, Ph.D. Thesis, University of Oviedo, Spain, 2008.
- [23] V.G. Pangarkar, A.A. Yawalkar, M.M. Sharma, A.A.C.M. Beenackers, Ind. Eng. Chem. Res. 41 (2002) 4141.
- [24] H.S. Fogler, Elements of Chemical Reaction Engineering, Prentice-Hall, Englewood Cliffs NJ, 1999 (chapter 11).
- [25] B.W. Hoffer, P.H.J. Schoenmakers, P.R.M. Mooijman, G.M. Hamminga, R.J. Berger, A.D. van Langeveld, J.A. Moulijn, Chem. Eng. Sci. 59 (2004) 259.
- [26] E. López, S. Ordóñez, F.V. Díez, H. Sastre, J. Hazard. Mater. 97 (2003) 281.
- [27] O. Levenspiel, Chemical Reaction Engineering, 3rd ed., Wiley, New York, 1999.
- [28] S. Kovenklioglu, Z. Cao, R.J. Ferrauto, E.N. Balko, AIChE J. 38 (1992) 1003.
- [29] S. Ordóñez, P. Hurtado, H. Sastre, F.V. Díez, Appl. Catal. A 259 (2004) 41.
- [30] G.C. Hadjilouzou, J.B. Butt, J.S. Dranoff, J. Catal. 131 (1991) 545.
- [31] C. Xia, J. Xu, W. Wu, X. Liang, Catal. Commun. 5 (2004) 383.
- [32] G. Yuan, M.A. Keane, J. Catal. 225 (2004) 510.
- [33] W.W. McNab, R. Ruiz, M. Reinhard, Environ. Sci. Technol. 34 (2000) 149.
- [34] N. Munakata, M. Reinhard, Appl. Catal. B 75 (2007) 1.
- [35] D. Angeles-Wadler, K. Mackenzie, F.D. Kopinke, Appl. Catal. B 90 (2009) 613.

- [36] H. Hildebrand, K. Mackenzie, F.D. Kopinke, *Appl. Catal. B* 91 (2009) 389.
- [37] C. Schüth, M. Reinhard, *Chemosphere* 38 (1995) 2897.
- [38] M.A. Aramendia, V. Borau, I.M. García IM, C. Jimenez, F. Lafont, A. Marinas, J.M. Marinas, F.J. Urbano, *J. Mol. Catal. A* 184 (2002) 237.
- [39] M. Sanchez, A. Hadasch, R.T. Fell, B. Meunier, *J. Catal.* 202 (2001) 177.
- [40] M.A. Aramendia, R. Burch, I.M. García, A. Marinas, J.M. Marinas, B.W.L. Southward, F.J. Urbano, *Appl. Catal. B* 31 (2001) 163.
- [41] J.M. Moreno, M.A. Aramendia, A. Marinas, J.M. Marinas, F.J. Urbano, *Appl. Catal. B* 76 (2007) 34.
- [42] J.M. Moreno, M.A. Aramendia, A. Marinas, J.M. Marinas, F.J. Urbano, *Appl. Catal. B* 59 (2005) 275.
- [43] R.F. Bueres, E. Asedegbega-Nieto, E. Díaz, S. Ordóñez, F.V. Díez, *Catal. Commun.* 9 (2008) 2080.
- [44] L. Gomez-Sainero, X.L. Seoane, J.L.G. Fierro, A. Arcoya, *J. Catal.* 209 (2002) 279.
- [45] C.H. Gammons, *Geochim. Cosmochim. Acta* 60 (1996) 1683.
- [46] Z. Karpinski, *Adv. Catal.* 37 (1990) 45.
- [47] P. Gelin, M. Primet, *Appl. Catal. B* 39 (2002) 1.
- [48] P. Hurtado, S. Ordóñez, H. Sastre, F.V. Díez, *Appl. Catal. B* 47 (2004) 85.
- [49] E. Díaz, S. Ordóñez, A. Vega, J. Coca, *J. Chromatogr. A* 1049 (2004) 139.
- [50] E. Díaz, S. Ordóñez, A. Vega, J. Coca, *Microporous Mesoporous Mater.* 82 (2005) 173.
- [51] J.M.A. Harssen, L. Jelemensky, P.J.M. Van Andel-Scheffer, B.F.M. Kuster, G.B. Marin, *Appl. Catal. A* 165 (1997) 499.
- [52] A. Cabiác, T. Cacciaguerra, P. Trens, R. Durand, G. Delahay, A. Medevielle, D. Plée, B. Coq, *Appl. Catal. A* 340 (2008) 229.